



New Solutions to Hazardous Waste Problems

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Attn: Anna Palmisano
Ref: Contract N00014-96-C-0370

May 29, 1997

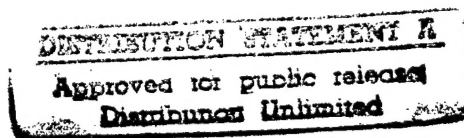
Dr. Palmisano:

Enclosed is a copy of the second quarter's progress report (CLIN # 0002) for the SBIR Phase II Project # N00014-96-C-0370 entitled "Development of Biotrickling Filters to Treat Sulfur and VOC Emissions." **Please note that Figures 6 and 7 of the report are Confidential and Proprietary.** A copy of this transmittal letter has been sent to Anna M. Weston, the Administrative Contracting Officer. In addition, one copy of the report was also sent to the Director of the Naval Research Laboratory, and two copies of the report were sent to DTIC.

With kindest regards,

A handwritten signature in cursive script, appearing to read 'A. Paul Togna'.

A. Paul Togna, Ph.D.
Manager, Air & Water Systems Development



cc: Anna M. Weston (ONR Contracting Officer)
Director of the Naval Research Laboratory
DTIC
Bill Guarini (Envirogen)
Yonghua Yang, Ph.D. (Envirogen)

Encl.

2nd Quarter Progress Report: December 31, 1996 to March 31, 1997
Months 4 to 6 - Phase II SBIR CLIN # 0002
Development of Biotrickling Filters to Treat Sulfur and VOC Emissions
Contract # N00014-96-C-0370

Attn: Anna Palmisano, Program Officer

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Background

The Phase II project was initiated on September 30, 1996. The goal of this SBIR project is to develop a cost-effective, efficient biological treatment system, a *biotrickling filter*, to treat air emissions of significance to the Navy. These emissions include odors from oily bilge holding tanks, and point sources of hazardous air pollutants (HAPs) such as paint spray booths. Biotrickling filters are similar to scrubbers, but rely on microorganisms on the packing surface to remove and degrade the contaminants.

Phase I work identified microbial cultures capable of degrading and growing on air pollutants of importance to the Navy. Greater than 98 percent hydrogen sulfide and methyl mercaptan removal efficiencies were demonstrated for odor applications, and 90 percent VOC (toluene, xylene, MEK, and n-butyl acetate) removal efficiencies were demonstrated for paint-spray booth applications. In addition, three different biomass support packing materials were screened.

The objectives of Phase II are to: (1) develop a method to control biofilm growth; (2) establish the full-scale system pressure drop characteristics; (3) establish the effective treatment range; (4) perform overall mass balances and confirm transformation to benign products; (5) demonstrate the technology in the field at a Navy site; and (6) prepare a final report detailing the results and conclusions of the Phase II effort, including an economic analysis.

Progress to Date

Objective 1 - Develop operating conditions that biologically lead to stable biofilm development and near-complete conversion of contaminant carbon to CO₂

The purpose of Objective 1 is to develop operating conditions that minimize biomass growth and maximize carbon conversion to carbon dioxide (CO₂). In order to accomplish this objective, biomass will be grown within the bench-scale systems used during Phase I until a high pressure drop is observed. System adjustments will then be made in order to decrease and stabilize the pressure drop while maintaining high contaminant removal efficiencies.

The biotrickling filter columns used during Phase I were cleaned and filled with similar packing materials that were used during Phase I. Two sets of columns are being operated: (1) an experimental set; and (2) a control set. The experimental set of columns will be manipulated, while the control set will not. The two sets of columns are labeled A1, A2, and A3 (System A - experimental columns) and B1, B2, and B3 (System B - control columns). Columns A1 and B1

have been filled with 16 mm (5/8") polypropylene Bio-PacTM from NSW (NSW Corporation, Roanoke, VA). This packing is very similar to the polypropylene PallTM rings used during Phase I, but costs significantly less, and is therefore an economical substitute. Columns A2 and B2 have been filled with a 50/50 (vol/vol) mixture of 25 mm (1") polypropylene Bio-PacTM and 13 mm (1/2") SIF[®] polyurethane foam cubes (Foamex International Inc., Eddystone, PA), similar to the mixture used during Phase I. Columns A3 and B3 contain the plastic cooler tower packing (Delta Cooling Towers, Inc., Fairfield, NJ) used during Phase I. The air flow is such that a vapor contact time of 40 seconds is achieved through each system. The contaminated vapor streams are created by adding a liquid contaminant mixture to the influent air stream using syringe pumps. The contaminant mixture contains: (1) methyl ethyl ketone (MEK), (2) toluene, (3) n-butyl acetate (nBA), and (4) xylenes. Each system has an inlet and outlet vapor sample line connected directly to a gas chromatograph (as described in the Phase I final report) for analysis of inlet and outlet vapor concentrations. Each system also has an inlet and outlet vapor sample line connected directly to a CO₂ analyzer.

The physical set-up of the systems was completed by the end of November. Influent stability tests were completed by the first week of December, and abiotic loss tests were completed by mid-January. The biotrickling filter columns were inoculated on January 17, 1997 with the cultures developed during Phase I. The influent feed concentration of each of the target contaminants was maintained at approximately 150 µg/L. By the end of February, heavy biomass growth and high pressure drops across the packing materials were observed. On February 25, 1997, the contaminant feed to both sets of columns was stopped. Three days later, on February 28th, and then again on March 4th (7 days after stopping the contaminant feed), the System A columns were inoculated with activated sludge from two local wastewater treatment plants in an attempt to provide higher microorganisms to aid in biomass consumption and stability. In addition, potassium was removed from the media feed to the System A columns on March 5th, 8 days after stopping the contaminant feed. Potassium remained in the feed to the System B columns. Potassium limitations have been shown to aid in controlling biomass growth in biotrickling filter columns (Holubar, P., C. Andorfer, and R. Braun, "Prevention of Clogging in Trickling Filters for Purification of Hydrocarbon-Contaminated Waste Air," *Proceedings of the 1995 Conference on Biofiltration, University of Southern California*, October 5-6, 1995, pp. 115-121). The potassium concentrations in the recirculating liquid over time within Columns A1 through A3 are plotted in Figure 1.

Both sets of columns (Systems A and B) exhibited a steady pressure drop reduction after the contaminant feed was stopped, as shown in the attached Figures 2 and 3. After 2 weeks, the pressure drop across the packing in both sets of columns was reduced to low levels (approximately 0.5 "H₂O or lower). In addition, the reduction in pressure drop across each system was directly correlated with CO₂ evolution, as shown in Figures 4 and 5, indicating that biomass consumption, i.e., endogenous respiration, was responsible for the decrease in pressure drop, as anticipated.

Approximately 16 days after stopping the contaminant feed, continuous contaminant addition was again resumed. The concentration of each contaminant was maintained at 100 to 125 µg/L

in the feed. On March 16, 1997, intermittent contaminant feeding was initiated to mimic typical paint spray booth operating schedules. Contaminants were added to the systems between 8:00 a.m. and 1:00 p.m. (5 hour operating schedule) Monday through Friday (5 day operating schedule). The concentration of each of the 4 contaminants was maintained between 100 and 125 $\mu\text{g/L}$. This feeding schedule was maintained for 6 weeks, with no noticeable increase in pressure drop across any of the columns (see Figures 2 and 3). The average performance of each of the systems is shown in Table 1. The 16 mm (5/8") polypropylene Bio-PacTM from NSW (NSW Corporation, Roanoke, VA) shows the best overall performance, with an average total VOC removal efficiency of approximately 85% for System A1 and B1.

Table 1. Average Contaminant Removal Efficiencies (Percent Removal)

Column	MEK	Toluene	n-BA	m-, p-Xylene	o-Xylene
A1	96	78	91	75	69
A2	93	52	90	49	47
A3	92	32	88	25	28
B1	90	89	85	82	79
B2	92	76	91	69	63
B3	91	74	87	59	55

Conclusions: It appears that biomass growth within biotrickling filters can be controlled effectively if the contaminant supply to the systems is intermittent, as is the case for spray booth discharge streams. The effects of activated sludge addition and potassium limitation on biomass growth is either not significant under the conditions tested, or is masked by the intermittent contaminant feed.

On May 5, 1997, intermittent operation was discontinued, and continuous addition of contaminants to the systems was initiated in order to perform systems mass balances.

Objective 2 - Establish the pressure drop characteristics of the two most optimal biomass support packing materials under full-scale system operating conditions

The purpose of Objective 2 is to establish the pressure drop characteristics of the two optimal biomass support packing materials under full-scale system operating conditions, using the shear forces of the vapor and liquid flowing through the column to control biomass growth. This

testing is being conducted in a 34 cm (1.13 ft) diameter polyvinyl chloride (PVC) biotrickling filter system. The packing height is approximately 1.2 meters (4 ft). For each of the packing materials being tested, four different air velocities will be evaluated: 0.15, 0.30, 0.46, and 0.61 m/s (30, 60, 90, and 120 cfm/ft²). At each air velocity, six liquid recirculation rates will be evaluated: 1.4, 3.4, 6.8, 10.2, 13.6, and 17.0 L/sec•m² (2, 5, 10, 15, 20, and 25 gpm/ft²). Ethanol is being supplied in the inlet air as the substrate for biomass growth. The inlet ethanol concentration is adjusted to provide an excess of ethanol in the effluent vapor from the reactor. The biotrickling filter system must be supplied an excess of nutrients and ethanol to ensure that biomass growth is limited only by the mechanical shear forces of the liquid and vapor.

The first packing material being testing is 25 mm (1") NSW polypropylene Bio-Pac™. The column containing the dumped packing material during Phase I, 16 mm plastic Pall™ rings, showed the best overall performance. 25 mm Bio-Pac™ is being tested instead of 16 mm Pall™ rings because for full-scale system applications, 16 mm packing would easily plug with biomass, and Bio-Pac™ is much less expensive than Pall™ rings. Testing of this packing material is nearly complete. Results are shown in Figures 6 and 7.

Objective 5 - Perform a field-pilot demonstration at a site chosen by the Navy to confirm the technical and economic competitiveness of the technology

Mr. Bill Guarini and Dr. Paul Togna have proceeded with Task 1 - Site Selection, of Objective 5. The purpose of these early site visits was to obtain paint spray booth operating data from the individual sites in order to determine which potential sites are appropriate for the demonstration. The three sites visited were (1) North Island Naval Air Station in San Diego, CA, a NELP site; (2) Lakehurst Naval Air Engineering Station in Lakehurst, NJ; and (3) Mayport Naval Station in Jacksonville, FL, also a NELP site. The base contacts at the three sites were: (1) Mr. Ed Bonnes at North Island; (2) Ms. Jill Sarafin at Lakehurst; and (3) Mr. Bob Tierney at Mayport. All of the individuals were very friendly and cooperative, and supplied Envirogen with the required data. The data from the sites were correlated and ranked in order of preference. A meeting was held at ONR on Friday, April 4, 1997 to discuss the three sites. In attendance at the meeting were Anna Palmisano, Allana Mitchell, Jeff Marquess, and Alex Lardis. Based on the operating schedules of the candidate spray booths and the anticipated discharge concentrations and compositions, the North Island Naval Air Station site was ranked first. Figures 8 and 9 show the anticipated discharge profile for the two candidate spray booths at the North Island site. It was agreed at the meeting that the North Island site was most appropriate for the demonstration, and Envirogen is proceeding with plans to perform the demonstration at the North Island site.

Schedule

Objective 1 - Develop operating conditions that biologically lead to stable biofilm development and near-complete conversion of contaminant carbon to CO₂

On schedule.

Objective 2 - Establish the pressure drop characteristics of the two most optimal biomass support packing materials under full-scale system operating conditions

On schedule.

Objective 5 - Perform a field-pilot demonstration at a site chosen by the Navy to confirm the technical and economic competitiveness of the technology

Objective 5 was to start approximately 1 year into the contract. However, we felt that it would be prudent to start the Site Selection process as soon as possible, and have therefore initiated Task 1.

Potassium Concentrations

Systems A1, A2, A3

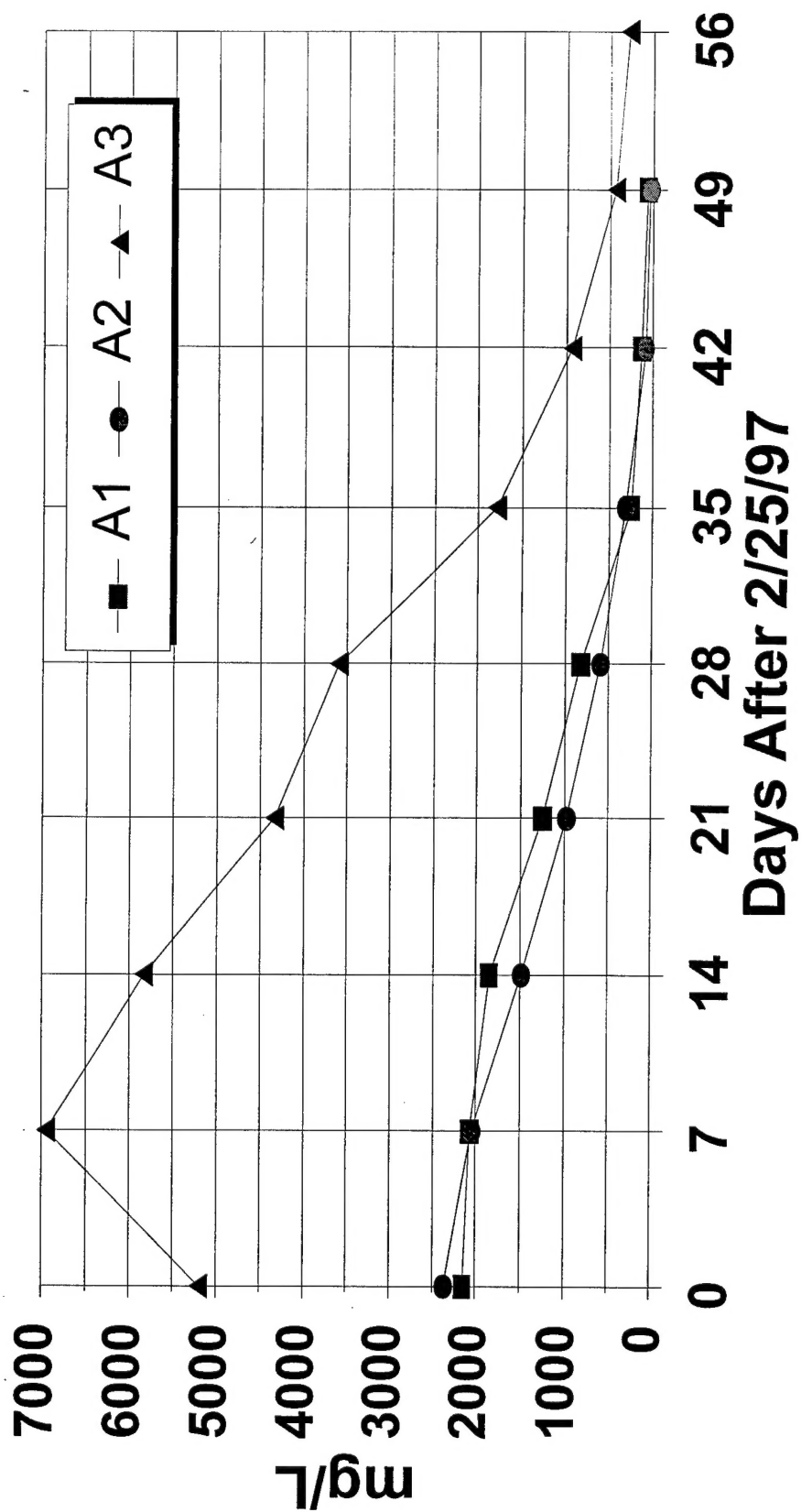


Figure 1

Pressure Drop

Systems A1, A2 and A3

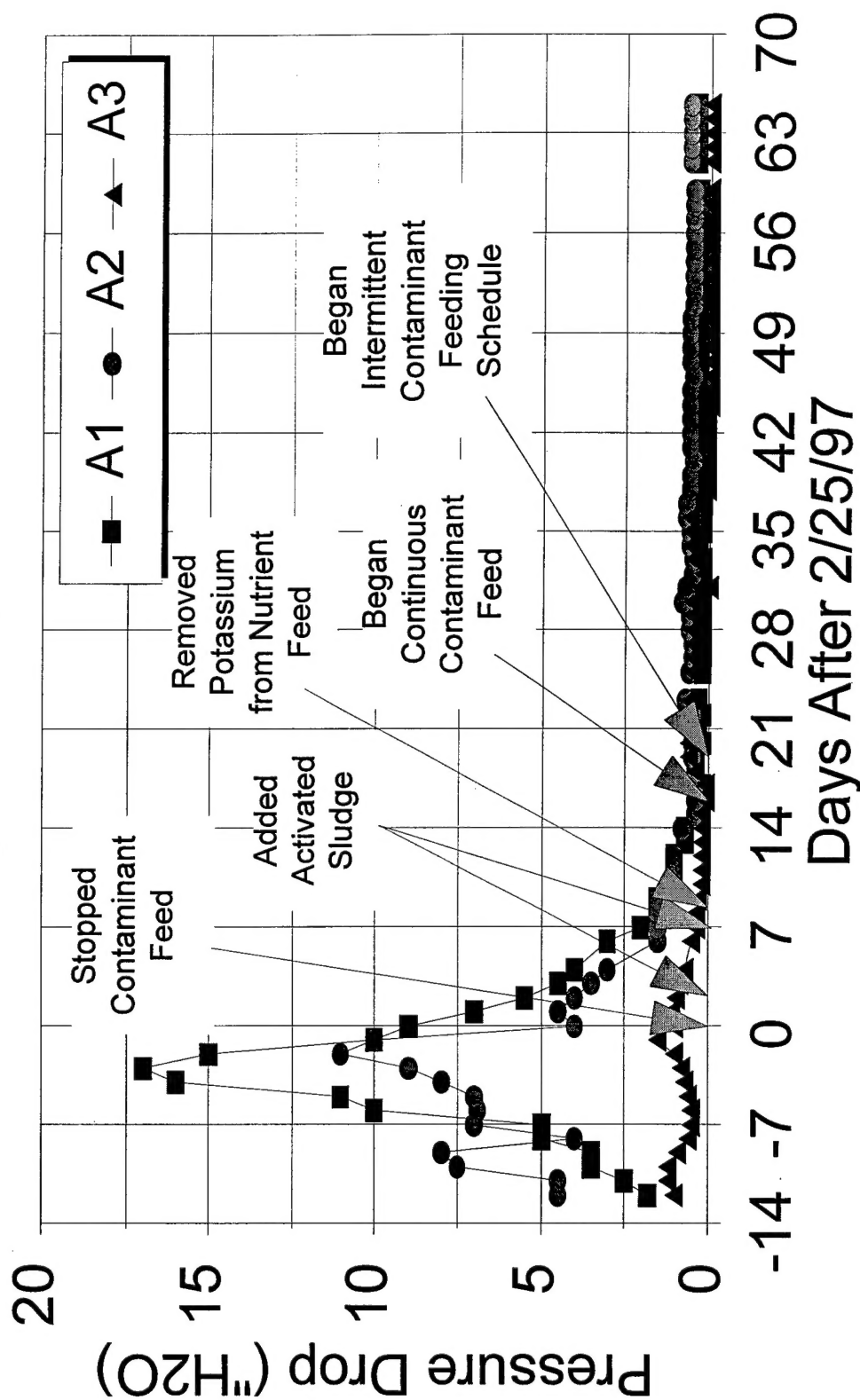


Figure 2

Pressure Drop

Systems B1, B2 and B3

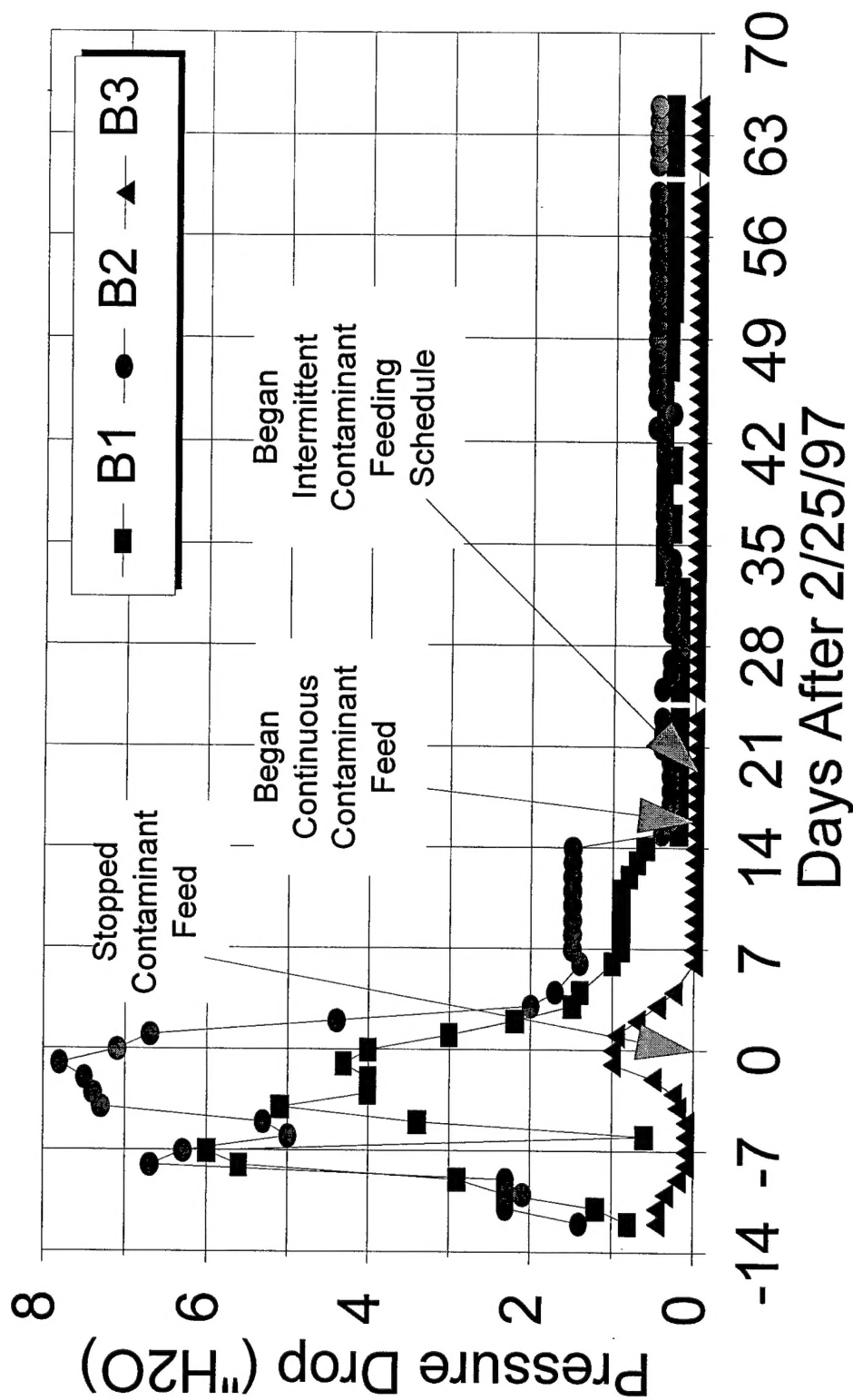


Figure 3

CO2 Concentrations

Biotrickling Filters A1, A2 and A3

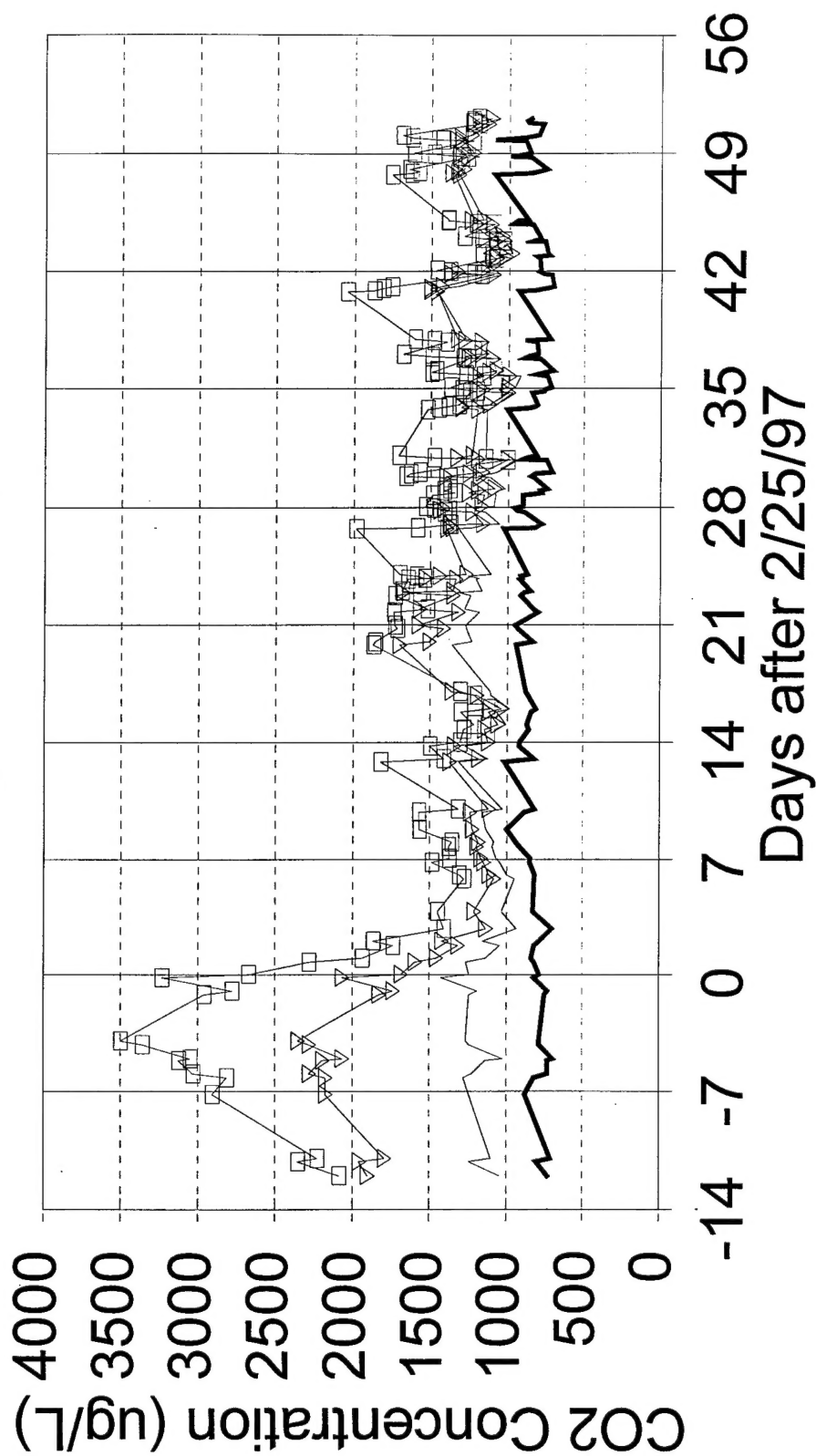


Figure 4

CO2 Concentrations

Biotrickling Filters B1, B2 and B3

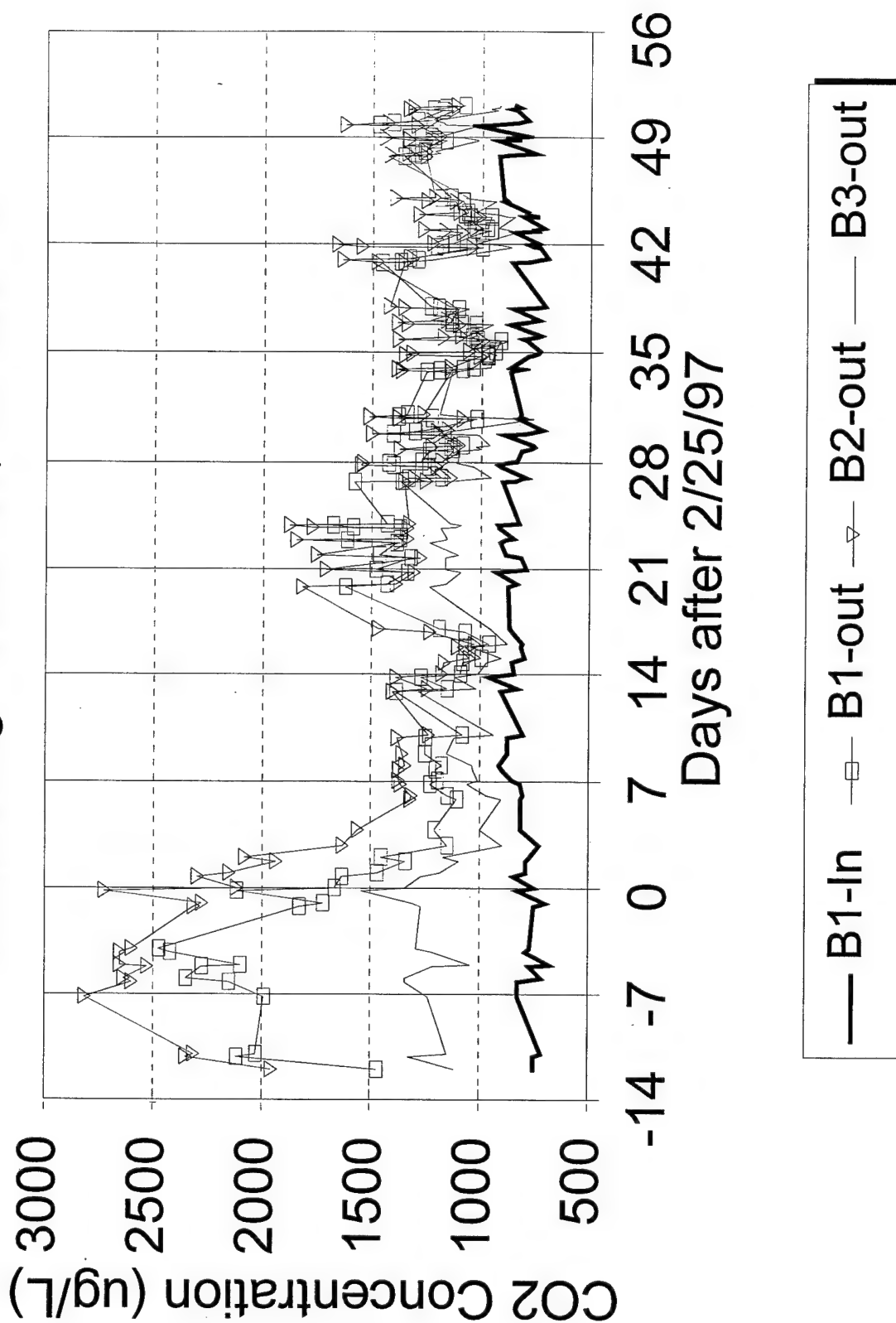


Figure 5

Pressure Drop VS Liquid Recirc. Rate

Ethanol Biotrickling Filter

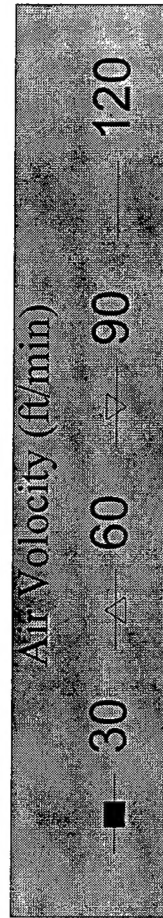
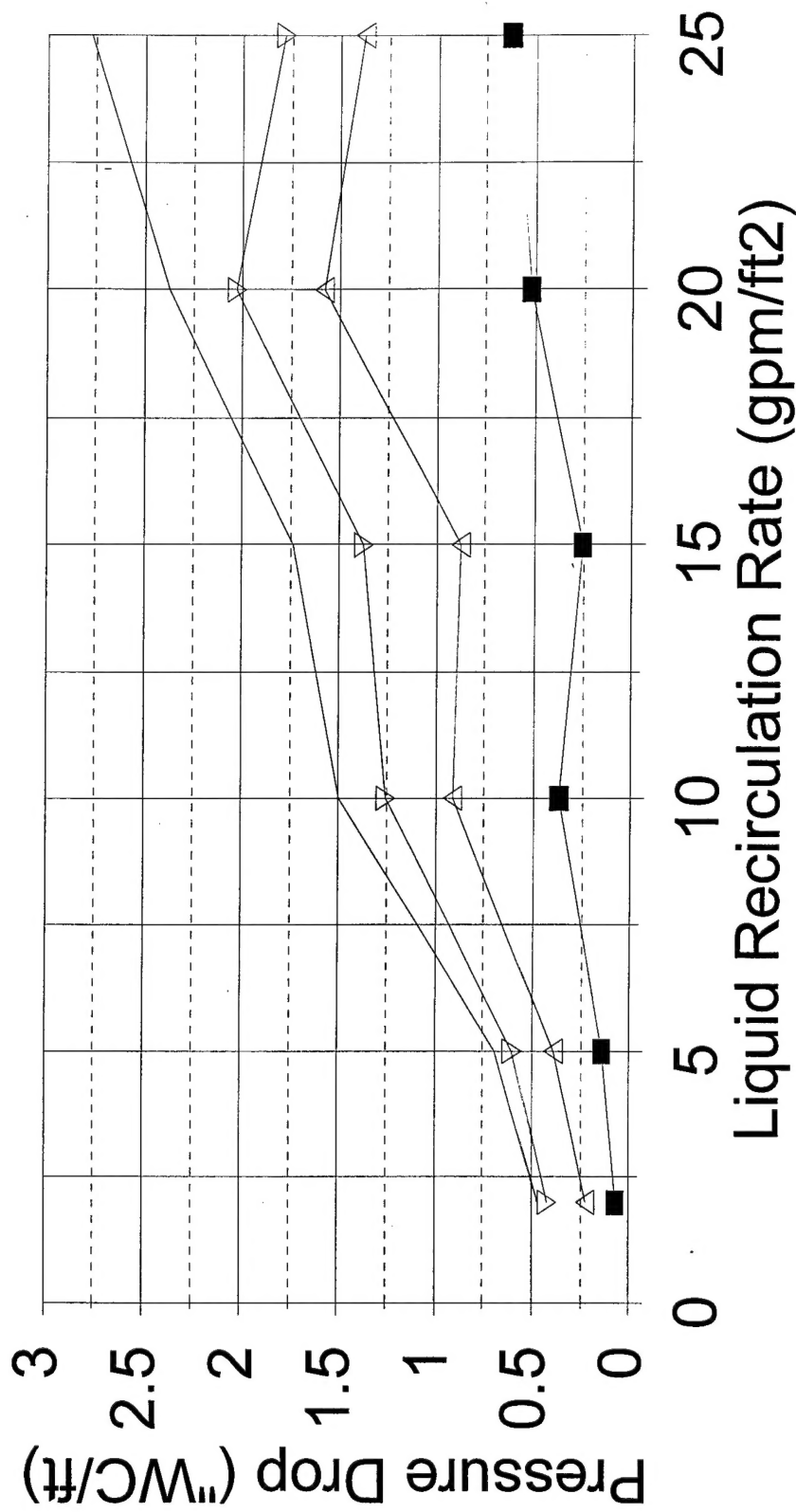


Figure 6

Pressure Drop vs Air Velocity

Ethanol Biotrickling Filter

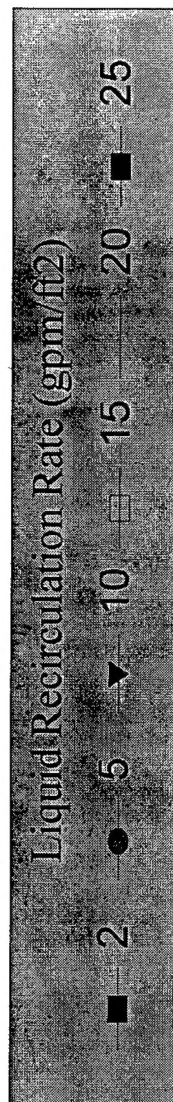
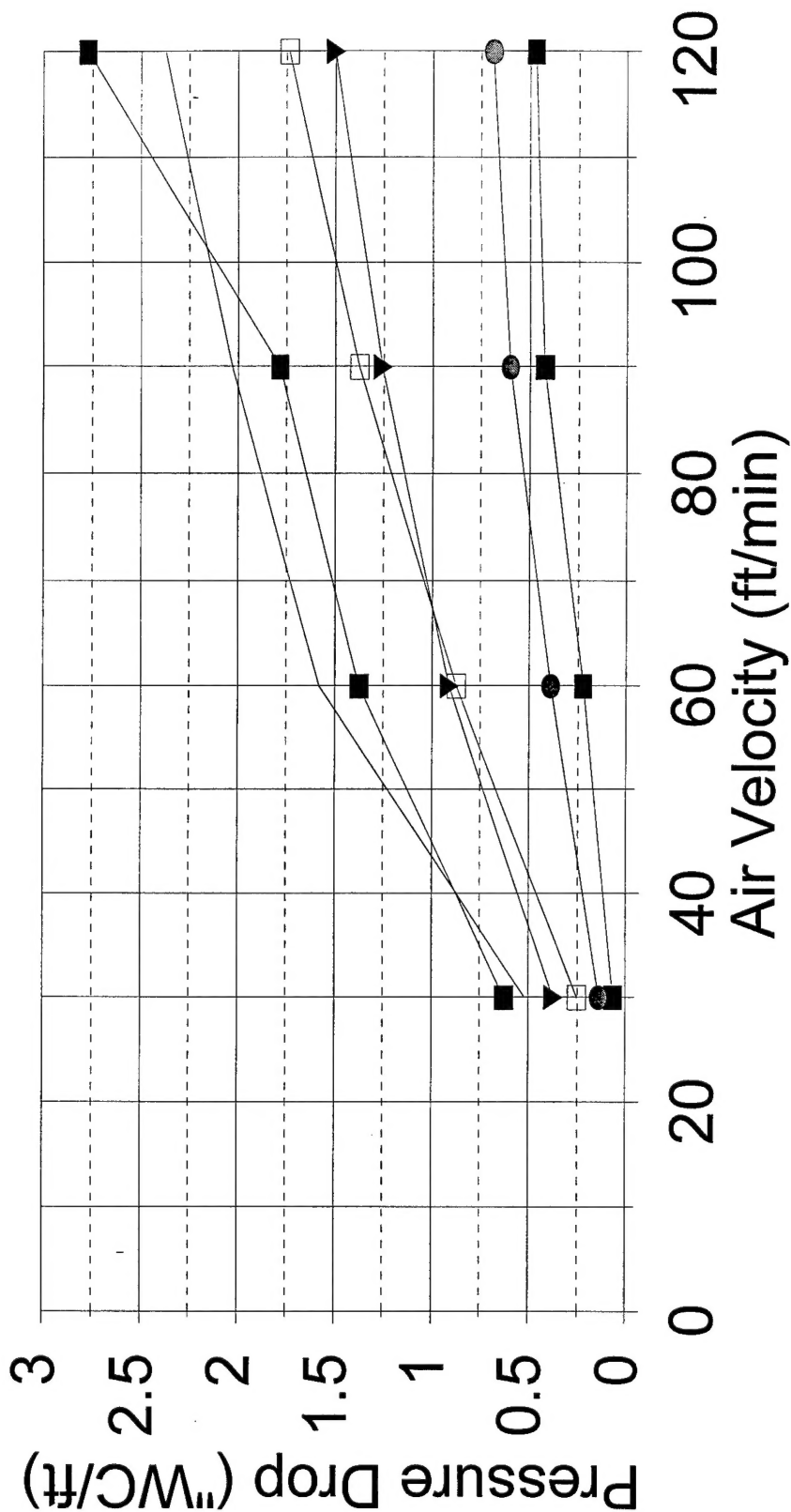


Figure 7

Typical Effluent over 3 Days in 1996

Building 305A Booth, San Diego, CA

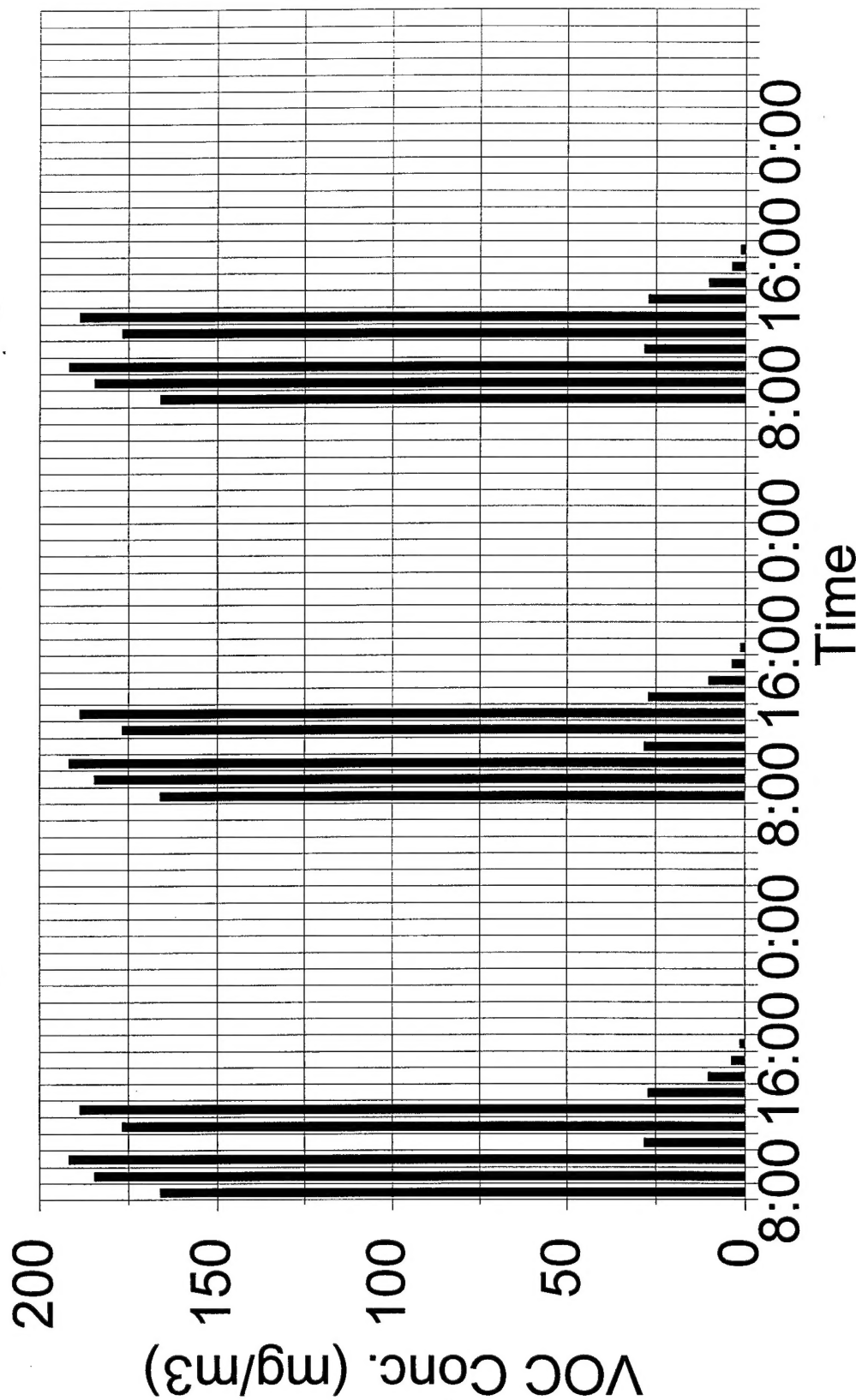


Figure 8

Typical Effluent over 3 Days in 1996

Building 305B Booth, San Diego, CA

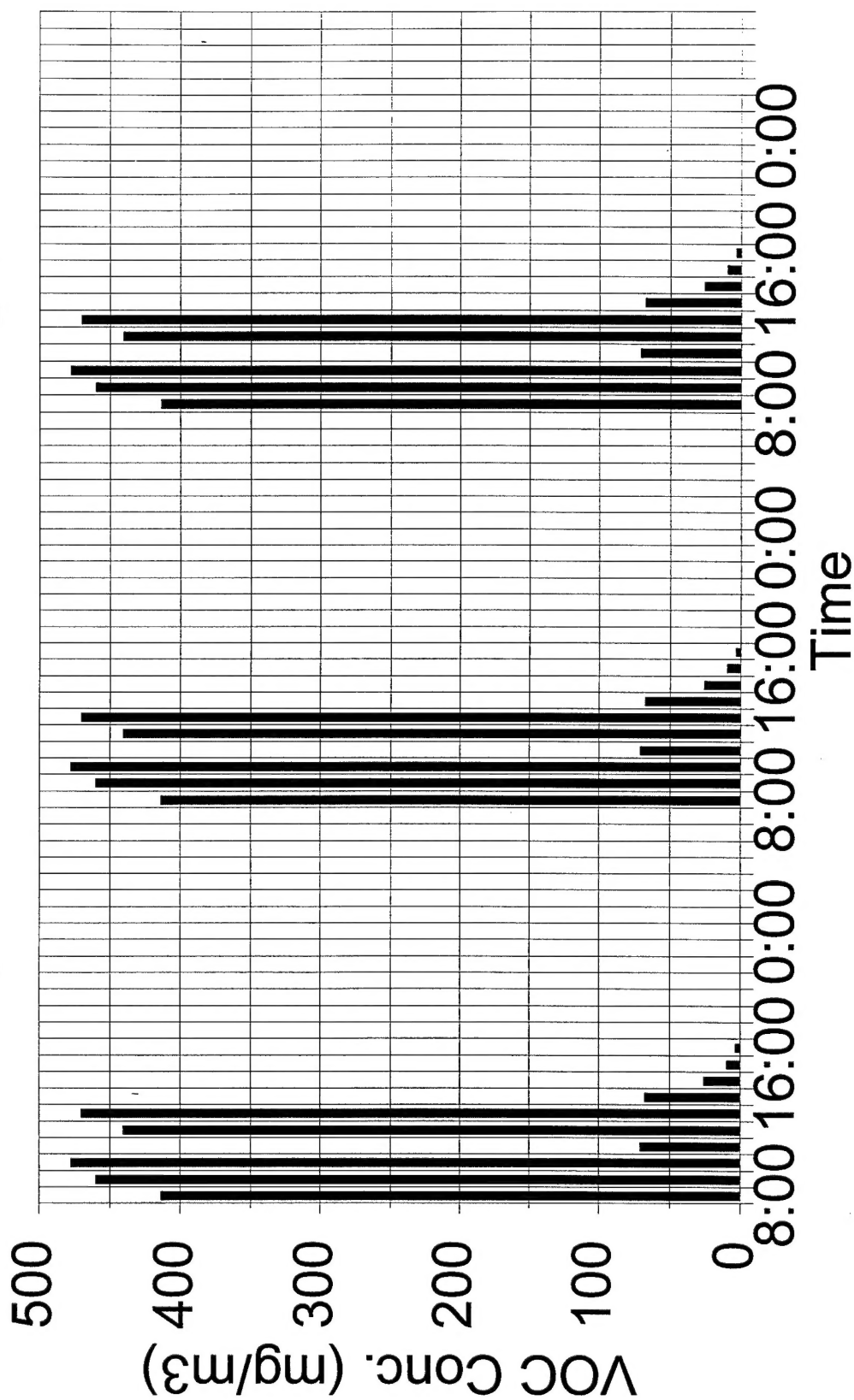


Figure 9